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NEW USSR METHOD OF PRODUCING SODIUM HYDROXIDE

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[Comment: Figures are appended. Numbers in parentheses refer to authors' bibliography.]

The accepted practical methods of producing sodium hydroxide (the lime and ferrite methods), at present, require a relatively costly chemical, i.e., calcined soda. The electrolytic method requires cheap electrical energy and is economically justified only when there are consumers for the chlorine which forms as a by-product.

Sodium sulfate (mirabilite) serves as the initial raw material in the method developed by us. As is known, sodium sulfide (1,2) is obtained from sodium sulfate at temperatures of 850 to 1,000° by reductive calcination. As a desulfurizing agent (3) we chose manganese dioxide ore which, as is known, contains a high percentage of MnO<sub>2</sub>.

During the investigation of this process it became apparent that other oxidized manganese ores could be used in the desulfurization. However, using these ores prolonged the reaction time.

We added a predetermined quantity of crushed dioxide ore to the solution of sodium sulfide in the reactor and started the agitator. After mixing, the contents of the flask were allowed to settle. This settling of the suspension proceeded satisfactorily. Under laboratory conditions, complete precipitation of the solid phase occurred within 20 minutes.

We analyzed the resulting caustic lye for the Na<sub>2</sub>S content and other sulfur salts (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> + Na<sub>2</sub>SO<sub>3</sub>) (4,5); we also determined the manganese content by the qualitative method (6).

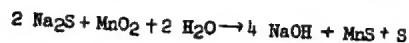
After the settling, we separated the caustic lye from the precipitate. We carefully washed the latter and then determined the amount of manganese sulfide in it. (7) To do this, we added hydrochloric acid to the precipitate in a hermetically sealed flask and passed an inert gas through the flask. If manganese sulfide was present, hydrogen sulfide was evolved. This was absorbed by a 2% solution of cadmium acetate (in the solid phase a precipitate of yellow-colored cadmium sulfide formed).

We studied the effects of the following factors on the reaction between the solution of sodium sulfide and the dioxide ore: temperature, the ratio of Na<sub>2</sub>S to MnO<sub>2</sub>, the concentration of the solution of sodium sulfide, time, the fineness of the ground dioxide ore, mixing, and the addition of the ore in separate small portions.

To establish the optimum temperature, we varied this factor from room temperature to 100°C. In this way it was determined that the degree of desulfurization (which corresponds to the degree of caustification) was greater at low temperatures than at high temperatures. We selected 18-25° as the optimum temperature.

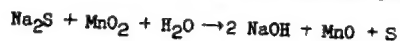
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The ratio of  $\text{Na}_2\text{S}$  to  $\text{MnO}_2$  exerts a great influence on the process. As is shown by an analysis of the solution and the precipitate, the following reaction takes place when the compounds indicated are present in an equimolecular ratio:



With this ratio of  $\text{Na}_2\text{S}$  to  $\text{MnO}_2$  we have the sulfide not only in the precipitate but also in the solution, which is undesirable.

To eliminate completely the sulfide from the caustic, it is necessary to use the proportion of  $\text{Na}_2\text{S} : \text{MnO}_2 = 1 : 1.5$ . With this ratio of  $\text{Na}_2\text{S}$  to  $\text{MnO}_2$  and other optimum conditions, the reaction proceeds in the following manner:



Sulfide is then found neither in the solution nor in the precipitate.

It follows that an excess of  $\text{MnO}_2$  should be used, and that the optimum ratio of  $\text{Na}_2\text{S} : \text{MnO}_2 = 1:1.5$ .

From what has been said above, it also follows that the reaction of sodium sulfide with manganese dioxide first produces manganese sulfide, which is then converted into sulfur in the presence of an excess amount of  $\text{MnO}_2$ .

The concentration of sodium sulfide, which in our experiment we changed from 5% to 15.5%, also exerted a great influence on the process of desulfurization (caustification). It must be kept in mind that with a relatively low concentration of sodium sulfide the conversion proceeds intensively. However, a dilute solution of sodium hydroxide is obtained and this is not desirable. On the other hand, a very high concentration of sodium sulfide should also not be used since, in the process of the reaction with the  $\text{MnO}_2$ , the sufficiently viscous solution of  $\text{Na}_2\text{S}$  is converted to a still more viscous solution of  $\text{NaOH}$ . This solution will coat the particles of  $\text{MnO}_2$ , which will impede the process of diffusion and also the process of caustification.

Figure 2 shows the effect of the concentration of sodium sulfide on the desulfurization process. It is also evident from Figure 2 that the addition of dioxide ore in several portions increases the degree of desulfurization and in addition to that, makes it possible to use a higher concentration of sodium sulfide in the solution. By the continuous addition of small portions of dioxide ore to the sodium sulfide we succeeded in increasing the concentration of the initial solution to 11.5-12%.

Besides this, addition of dioxide ore in small portions results in intensive action during the process, and, consequently, decreases the necessary reaction time. Figure 3 shows the relation of time to the degree of desulfurization of sodium sulfide. As is apparent, not more than 2 hours are necessary for the desulfurization of the sodium sulfide.

On the basis of the experiments it was also established that treatment of a solution of sodium sulfide with manganese dioxide or other oxidized manganese ores should be carried out under energetic agitation. A particle size corresponding to 400 holes/cm<sup>2</sup> can be assumed as the optimum fineness of grinding.

The sodium hydroxide solution produced under optimum conditions has a concentration of 117-120 g/l and its composition satisfies the standard requirements.

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The solution of sodium hydroxide is subsequently treated by the following usual procedures: (a) evaporation to a desired concentration if it is to be used in the liquid state, or (b) fusing of the concentrated alkali if it is necessary to produce solid caustic. Furthermore, there is the possibility of using the sodium hydroxide solution which has been obtained directly in a number of industrial applications; for example, the manufacture of soap.

The method which we have developed for the production of sodium hydroxide requires no complicated operations and is extremely simple from the standpoint of requirements for equipment. (See the flowsheet in Figure 4.)

An approximate estimate of the prime cost showed the marked economic advantages of this method. (This report was submitted 30 November 1953 by Academician S. Ya. Vol'fkovich.)

[Appended figures follow:]

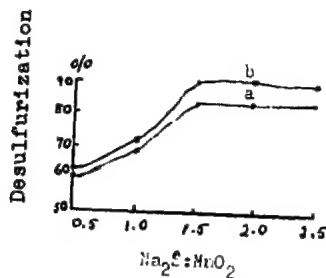


Figure 1. Effect of the Ratio  $\text{Na}_2\text{S}:\text{MnO}_2$

- a. Without agitation
- b. With agitation

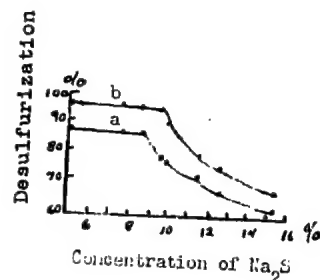


Figure 2. Effect of the Concentration of Sodium Sulfide

- a. When the entire amount of  $\text{MnO}_2$  is added in the beginning of the experiment
- b. When  $\text{MnO}_2$  is added in three portions

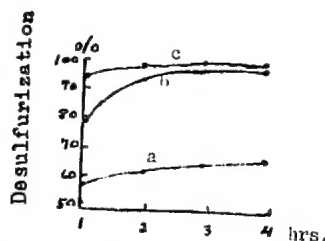


Figure 3. Effect of Time

- a. When the entire amount of manganese ore is added in the beginning of the experiment
- b. When the manganese ore is added in three portions
- c. When the manganese ore is added in six portions

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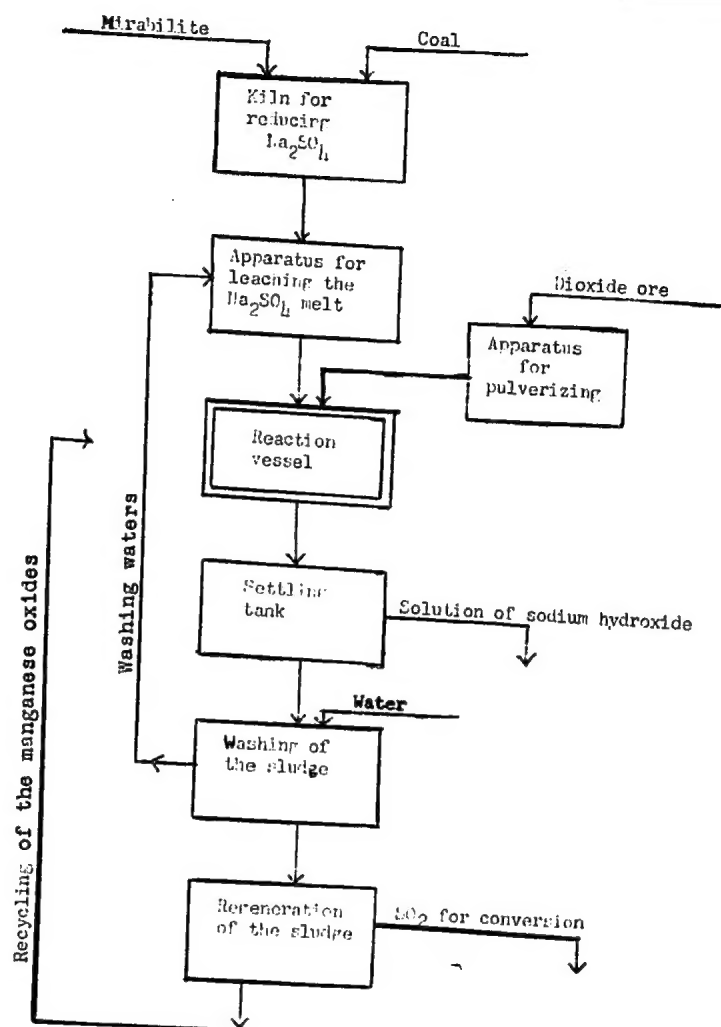


Figure 4. Scheme for the Production of Sodium Hydroxide from Mirabilite

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